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(71)Applicant : HITACHI LTD

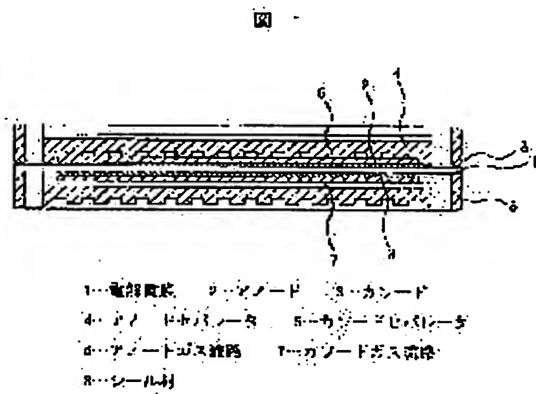
(72)Inventor : YAMAGA MASASHI
KAMO YUICHI

(54) PROTON CONDUCTIVE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To solve such a problem that since an existing electrolyte membrane for a fuel cell permeates methanol and a crossover is generated.

SOLUTION: This proton conductive material contains metal oxide hydrates in which the number of hydration is 1/2 to 5 per molecule and an organic material having proton conductivity, and is produced by dispersing the metal oxide hydrates into the organic material, and thereby, the methanol shut off property is enhanced, and in the case being used in the fuel cell supplying fuel containing methanol to an anode, drop in cell voltage caused by the crossover can be suppressed.



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CLAIMS

[Claim(s)]
[Claim 1] The proton conductivity ingredient with which it is the ingredient which this metallic-oxide hydrate is distributing to this organic material, and the hydration number per metallic-oxide 1 molecule is characterized by or more 1/2 being five or less including a metallic-oxide hydrate and the organic material which has proton conductivity.
[Claim 2] The proton conductivity ingredient according to claim 1 characterized by a metallic-oxide hydrate containing at least one element of Sn, Ti, and W.
[Claim 3] The proton conductivity ingredient according to claim 1 with which a metallic-oxide hydrate is characterized by being the content not more than more than 580wt% to the organic material which has proton conductivity.
[Claim 4] The fuel cell characterized by being the proton conductivity ingredient with which an electrolyte membrane is shown in claim 1 in the fuel cell with which the basic material is formed from the anode, cathode, and electrolyte membrane which are the reaction field to which an electrochemical oxidation reduction reaction advances.
[Claim 5] The production approach of the proton conductivity ingredient characterized by including the process at which the hydration number per molecule produces or more 1/2 metallic-oxide hydrate it is [hydrate] five or less, the process which mixes the produced metallic-oxide hydrate with the organic material which has proton conductivity, and the process which forms a metallic-oxide hydrate and the mixture of a proton conductivity organic material in the shape of a sheet.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the technical field about the generation-of-electrical-energy device which takes out energy using electrochemical reaction by making into oxidizing agent gas the gas which contains a fuel and oxygen for hydrogen or a hydrocarbon ingredient.
[0002]
[Description of the Prior Art] Telephone, a book type personal computer, an audio-visual device, or the information terminal equipment for mobile is miniaturized by advance of the latest electronic technique, and spread rapid as a portable electronic device is progressing by it. Conventionally, such a portable electronic device is a system driven with a rechargeable battery, and has developed into the nickel/Cd cell, the nickel / hydrogen cell, and also Li ion cell from the seal lead dc-battery with the appearance of a new style rechargeable battery, a miniaturization / lightweight-izing, and a high energy consistency-ized technique. Cell active material development for raising an energy density also in which rechargeable battery and development of high capacity cell structure are performed, and efforts to realize a power source with the more long time in 1 charge are paid.
[0003] However, as for a rechargeable battery, charging after the power activity of a constant rate is indispensable, and since a charging equipment and the comparatively long charging time are needed, many problems are left behind to long duration continuation actuation of a portable electronic device. From now on, the portable electronic device is going in the increasing amount of information and the direction which needs more the power source of a high energy consistency, i.e., the long power source of continuous duty time amount, with high power density corresponding to the improvement in the speed, and the need for the small generator (micro generator) which does not need charge is increasing.
[0004] A fuel cell power source can be considered as a thing corresponding to such a request. Since a fuel cell transforms into direct electrical energy electrochemically the chemical energy which a fuel has and does not need a power unit like the generator using internal combustion engines, such as the usual engine generator, the implementability as a small generation-of-electrical-energy device is high.
[0005] Moreover, a fuel cell becomes unnecessary [suspending actuation of a portable electronic device temporarily for charge which is seen in the case of a rechargeable battery], in order to continue a generation of electrical energy, as long as a fuel is supplied. Hydrogen gas is oxidized with an anode using the electrolyte membrane of perfluorocarbon-sulfonic-acid system resin in such a request, and the polymer electrolyte fuel cell (PEFC:Polymer Electrolyte Fuel Cell) which returns and generates oxygen with a cathode is known as a cell with high output density.
[0006] Although PEFC is used as hydrogen fuel, the direct handling of hydrogen gas has a problem in a safety aspect. Then, using hydrocarbon system fuels, such as alcohol, as a fuel, a refining reaction is made to generate hydrogen and the system which supplies the obtained hydrogen to a fuel cell is considered. Although the handling of a fuel is easy and a fuel-supply infrastructure is also practical as compared with hydrogen, since, as for a refining reaction, heat 250 degrees C or more is needed in this system, it is unsuitable for a portable way.
[0007] Then, examination of the type which uses liquid alcohol for a fuel and is supplied to a direct fuel cell is advanced. This type of fuel cell is called the methanol direct mold fuel cell (DMFC:Direct Methanol Fuel Cell). Especially since the refining machine which needs an elevated temperature will become unnecessary and the light weight of a system and simple-ization will be attained if the direct utilization of the liquid fuel can be carried out, promising ** is carried out as a power source of mobile computing devices.
[0008] However, the perfluorocarbon-sulfonic-acid system resin which was mentioned above and which is

an electrolyte ingredient has the large degree which absorbs a methanol, and, as for the resin which absorbed the methanol, a configuration changes with swelling. When perfluorocarbon-sulfonic-acid system resin is made into the shape of a film, the cutoff nature to a methanol is low, and the methanol contacted on one side will permeate and will penetrate the film to the field on a background.
[0009] When this ingredient is used as an electrolyte ingredient of DMFC, the methanol supplied to the anode which is a fuel electrode is penetrated from an anode on the film to the cathode which is an oxygen pole, as a result of permeating and swelling. Since the oxygen and the direct oxidation reaction which were supplied to the cathode will arise if the transmitted methanol reaches a cathode, the energy which can be taken out according to electrochemical reaction decreases. Consequently, the generation-of-electrical-energy electrical potential difference as a cell falls.
[0010] Therefore, in order to raise the engine performance of DMFC, development of the electrolyte ingredient which was excellent in methanol cutoff nature was needed.
[0011] By JP,2001-167775,A, the electrolyte membrane which was excellent in making an electrolyte membrane into the layer structure and using the low layer of ionic conduction nature as a surface layer at methanol cutoff nature is proposed about this technical problem. Moreover, in JP,10-40936,A, the structure which controlled osmosis in the counter electrode of a methanol by laying the oxidation catalyst layer for oxidizing a methanol underground into ion exchange membrane is proposed.
[0012] However, since the produced electrolyte membrane by the technique shown above served as the layer structure, the response over membranous thin-shape-izing also had the technical problem that it was difficult and fabrication manday increased as compared with the usual homogeneous membrane.
[0013] Moreover, for example by JP,2001-93543,A, in order to prevent a methanol crossover, the ingredient which made the organic material distribute the vitrified amorphous proton conductor containing an OH radical is proposed. However, the ingredient shown above needed elevated-temperature heat-treatment of 500 degrees C or more on the process which produces the ingredient which has the OH radical, and ingredient production by the low-temperature process was dramatically difficult.
[0014]
[Problem(s) to be Solved by the Invention] This invention is to offer the proton conductivity film whose methanol cutoff nature improved as compared with the conventional fluorine system. Moreover, it is in offer of the fuel cell which used the proton conductivity film and it producible in a low-temperature process 100 degrees C or less as an electrolyte ingredient.
[0015]
[Means for Solving the Problem] In this invention, in order to attain the above-mentioned technical problem, examination was promoted wholeheartedly, and when the electrolyte membrane was formed by making the organic material which has proton conductivity add and distribute the metallic-oxide hydrate the hydration number of whose is 1/2 to 5 per monad, it came to acquire knowledge that methanol cutoff nature improves dramatically.
[0016] A metallic-oxide hydrate has interlayer water or the water of adsorption, and a certain kind of the restraint or the interaction force over them of a metallic-oxide hydrate is dramatically strong.
[0017] This restraint also affects the proton company water which is the water molecule accompanied in case the proton generated with the anode of a fuel cell moves in the inside of the film. That is, if a metallic-oxide hydrate exists in an electrolyte membrane in the state of distribution, the water motion which moves in the inside of it will be controlled, and the effectiveness of reducing seemingly the water permeability which is the index which permeates and penetrates the film is shown. In this case, in order that a proton may carry out the hopping of the restrained water molecule and may move a charge, it has the description whose ionic conductivity is also an ingredient and equivalent extent conventionally.
[0018] Since the water molecule hydrated in the methanol in the electrolyte membrane is restrained with a metallic oxide when the ion conductivity organic material which distributed the metallic-oxide hydrate is used for an electrolyte ingredient, a fuel cell is assembled and a methanol water solution is supplied to the anode which is a fuel electrode, effect arises also in the methanol molecule loosely combined by hydration, and the amount of the methanol which penetrates the film to the cathode which is an oxygen pole as the result, and reaches it decreases. That is, in order that the amount of methanol crossovers may decrease, the cel sag of DMFC can be controlled and the good engine performance is demonstrated.
[0019] The ingredient which contains Sn, Ti, and at least one or more sorts of W elements as a metallic element of a metallic-oxide hydrate is desirable especially from a viewpoint of the restraint of a water molecule. Moreover, it is satisfactory even if it is elements including transition-metals elements, such as aluminum, Si, Sc, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Ga, germanium, As, Se, Y, Zr, Nb, Mo, Ru, Rh, Pd,

Ag, and In, in addition to this.
[0020] More than 1wt% of the content to the organic material of a metallic-oxide hydrate in which effectiveness shows up actually as methanol permeability is desirable. More than % [5wt] effect appears in the cel electrical potential difference of the cell which furthermore incorporated the electrolyte, it is still more desirable in it being.
[0021] On the other hand, if a metallic-oxide hydrate is made into high content, a physical hole will produce the opening formed by particles in an electrolyte membrane, without the ability finishing burying an organic material. If a hole is generated, mechanical strength will fall selectively and it will become the cause of a crack (divide). If a crack arises in an electrolyte membrane, a methanol will cross a direct cathode. Therefore, as an upper limit of the content to the organic material of a metallic-oxide hydrate, 80wt(s)% is desirable.
[0022] Although there will be especially no definition if it is the ingredient which has thermal resistance, acid resistance, and flexibility as an organic material which has ion conductivity, a dope or the ingredient combined and fixed chemically is desirable in the sulfonic acid of the polystyrene which carried out chemical modification further besides perfluorocarbon sulfonic acid, a polyether ketone, a polyether ether ketone, polysulfone, polyether sulphone, or other engineering-plastics ingredients, a phosphoric acid, and other proton carriers.
[0023]
[Embodiment of the Invention] Although an example explains this invention in more detail below, this invention is not limited to these.
[0024] (Example 1) The production approach of a tungstic oxide hydrate / perfluorocarbon-sulfonic-acid electrolyte membrane and an electrolyte membrane / electrode zygote is explained below as an example of this invention.
[0025] It was gradually dropped at 450ml3N HCl cooled at 5 degrees C, stirring 50ml of 1.0M Na2WO3 water solutions with a magnetic stirrer, and yellow precipitate was obtained. 0.1N HCl 300ml after removing a supernatant In addition, it stirred for 10 minutes, and the supernatant was removed, after putting in order to make precipitate sediment.
[0026] Then, it was left for 24 hours, after adding 300ml pure water to precipitate and stirring for 10 minutes. The supernatant of the solution which powder sedimented and changed into the separation condition thoroughly was thrown away, and the pure water of tales doses was newly added. The same washing actuation was repeated 6 times and the impurity ion originating in an unreacted raw material was removed. The tungstic oxide hydrate was obtained by filtering after that. As for the precipitate produced by this approach, it was checked from X diffraction measurement, and thermo gravity and differential thermal analysis that it is tungstic oxide 2 hydrate.
[0027] It is a tungstic oxide hydrate to Nafion to a 5wt(s)% Nafion 117 alcoholic water solution (water, isopropanol, and normal propanol are the product made from mixed solvent:Fluka Chemika of 20:40:40 at a weight ratio) 4.5wt(s)% It added and the electrolytic solution was produced. It stirred heating an electrolytic solution at 40 degrees C, and the condition as it is was maintained for 120 minutes. On slide glass, with the applicator, the electrolytic solution after stirring was cast so that the thickness after desiccation might be set to 30 micrometers, and the electrolyte sheet was formed. After making it harden at a room temperature for 24 hours, it exfoliated from the glass substrate and the sheet was heat-treated at the temperature of 50 degrees C for 3 hours. Furthermore, the film after desiccation was immersed in 1M sulfuric acid for 8 hours, after performing sufficient rinsing, it was made to season naturally, and the electrolyte membrane was obtained.
[0028] Next, what added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts, and was kneaded in the shape of a paste was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. the amount of platinum support of the obtained anode -- about 0.5 mg/cm2 -- it is -- the amount of ruthenium support -- about 0.5 mg/cm2 it was . The Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts was added to the field of the opposite hand of the formed electrolyte membrane, what was kneaded in the shape of a paste was applied to it so that the thickness at the time of desiccation might be set to 15 micrometers, and it might lap with an anode, and it dried to it at 60 degrees C for 3 hours, the cathode was formed in it, and the electrolyte membrane / electrode zygote was produced. the amount of platinum support of the obtained cathode -- about 0.3 mg/cm2 it was . The zygote after desiccation was

immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.
[0029] (Example 2) The production approach of a titanium oxide hydrate / perfluorocarbon-sulfonic-acid electrolyte membrane and an electrolyte membrane / electrode zygote is explained below as an example of this invention. It heated at 80 degrees C, making 5g of titanium metal powder react to hydrogen peroxide solution 30%, and 240-hour stirring and after making it dissolve, the peroxide which removes an unreacted object by filtration and serves as a precursor was produced.
[0030] After adding a 5-N caustic-alkali-of-sodium (NaOH) water solution to the obtained water solution, 6-N hydrochloric acid was added and precipitate was obtained. This sediment was filtered and it was made to dry in a desiccator. 400ml pure water was added to 5g of desiccation powder obtained by the above-mentioned approach, and it stirred for 30 minutes to it, and was left to it for 24 hours. The supernatant of the solution which powder sedimented and changed into the separation condition thoroughly was thrown away, and the pure water of tales doses was newly added. The same washing actuation was repeated 6 times, the impurity ion originating in an unreacted raw material was removed, and the titanium oxide hydrate was obtained. It became clear from thermogravimetric measurement that a hydration number was 2.
[0031] It is a titanium oxide hydrate to Nafion to a 5wt(s)% Nafion 117 alcoholic water solution 4.5wt(s)% It added and the electrolytic solution was produced. It stirred heating an electrolytic solution at 40 degrees C, and the condition as it is was maintained for 120 minutes. On slide glass, with the applicator, the electrolytic solution after stirring was cast so that the thickness after desiccation might be set to 30 micrometers, and the electrolyte sheet was formed. After making it harden at a room temperature for 24 hours, it exfoliated from the glass substrate and the sheet was heat-treated at the temperature of 50 degrees C for 3 hours. Furthermore, the film after desiccation was immersed in 1M sulfuric acid for 8 hours, after performing sufficient rinsing, it was made to season naturally, and the electrolyte membrane was obtained.
[0032] Next, what added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts, and was kneaded in the shape of a paste was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. the amount of platinum support of the obtained anode -- about 0.5 mg/cm2 -- it is -- the amount of ruthenium support -- about 0.5 mg/cm2 it was . The Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts was added to the field of the opposite hand of the formed electrolyte membrane, what was kneaded in the shape of a paste was applied to it so that the thickness at the time of desiccation might be set to 15 micrometers, and it might lap with an anode, and it dried to it at 60 degrees C for 3 hours, the cathode was formed in it, and the electrolyte membrane / electrode zygote was produced. The amounts of platinum support of the obtained cathode were about 0.3 mg/cm2. The zygote after desiccation was immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.
[0033] (Example 3) The production approach of a tin-oxide hydrate / sulfonation polyether sulphone electrolyte membrane and an electrolyte membrane / electrode zygote is explained below as another example of this invention.
[0034] 17.5g (SnCl4and5H2O) of stannic chlorides was dissolved in 50ml water, and it heated and hydrolyzed at 60 degrees C. Heated and riped for 1 hour, and filter the obtained precipitate, it was made to add aqueous ammonia to this and to dry at 95 degrees C, and the stannic-acid ghost hydrate (SnO2andnH2O) was obtained. n is about 1.8 from thermo gravity change measurement. It estimated. 400ml pure water was added to 10g of produced tin-oxide hydrates, and it stirred for 30 minutes to them, and was left in them for 24 hours. The supernatant of the tin-oxide hydrate sedimented and separated was extracted and thrown away, and the pure water of tales doses was newly added. The same washing actuation was repeated 6 times and the impurity ion originating in an unreacted raw material was removed. It was made to season naturally after washing processing, and used for subsequent electrolyte membrane production.
[0035] Polyether sulphone 0.5g which carried out desiccation processing It added to NMP (N-methyl pyrrolidone), and stirred at 25 degrees C for 2 hours, and the 5wt% solution was produced. 45ml of sulfuric acids was added to this solution, and heating stirring was carried out at 45 degrees C under the inert gas ambient atmosphere for 3 hours. It puts into an every reaction container degrees C [15 degrees C] water bath, 20ml of oleums is further added at 1ml a rate for /, and after addition termination is 1.5 further. Time amount continuation stirring was carried out and the sulfonation reaction was advanced. It was dropped at pure water with a rate of 2l. [per 5ml of solutions] obtained, and sulfonation polyether sulphone was

deposited. After washing by filtration and pure water, it was made to dry and the obtained deposit precipitate obtained sulfonation polyether sulphone. The ion exchange capacity of the obtained sulfonation polyether sulphone was 1.25 meq/g. Water, isopropanol, and normal propanol dissolved the sulfonation polyether sulphone produced by the above-mentioned approach in the mixed solvent of 20:40:40 by the weight ratio, and the 20wt% solution was adjusted.

[0036] To a 20wt% sulfonation polyether sulphone solution, it is the tin-oxide hydrate produced by the above-mentioned approach to sulfonation polyether sulphone 4.5wt(s)% It added so that it might become, and the electrolytic solution was produced. The electrolytic solution was stirred for 120 minutes in ordinary temperature. On slide glass, with the applicator, the electrolytic solution after stirring was cast so that the thickness after desiccation might be set to 30 micrometers, and the electrolyte sheet was formed. After making it hold at a room temperature for 24 hours, it heat-treated at the temperature of 50 degrees C for 3 hours. Made the sheet exfoliate from a substrate after that, after performing sufficient rinsing, it was made to season naturally, and the electrolyte membrane was obtained.

[0037] Next, what added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts, and was kneaded in the shape of a paste was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. the amount of platinum support of the obtained anode -- about 0.5 mg/cm2 -- it is -- the amount of ruthenium support -- about 0.5 mg/cm2 it was . The electrolyte membrane / electrode zygote was produced by adding the Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts to the field of the opposite hand of the formed electrolyte membrane, applying to it what was kneaded in the shape of a paste so that the thickness at the time of desiccation may be set to 15 micrometers, drying to it at 60 degrees C for 3 hours, and forming a cathode in it. The amounts of platinum support of the obtained cathode were about 0.3 mg/cm2. The zygote after desiccation was immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.

[0038] (Example 4) Another example of this invention is explained below.

[0039] 17.5g (SnCl4and5H2O) of stannic chlorides was dissolved in 50ml water, and it heated and hydrolyzed at 60 degrees C. Heated and riped for 1 hour, and filter the obtained precipitate, it was made to add aqueous ammonia to this and to dry at 95 degrees C, and the stannic-acid ghost hydrate (SnO2andnH2O) was obtained. n estimated it as about 1.8 from thermo gravity change measurement. 400ml pure water was added to 10g of produced tin-oxide hydrates, and it stirred for 30 minutes to them, and was left in them for 24 hours. The supernatant of the tin-oxide hydrate sedimented and separated was extracted and thrown away, and the pure water of tales doses was newly added. The same washing actuation was repeated 6 times and the impurity ion originating in an unreacted raw material was removed. It was made to season naturally after washing processing, and used for subsequent electrolyte membrane production.

[0040] The tin-oxide hydrate produced by the above-mentioned approach was added so that it might become the amount of 30wt% in a 5wt(s)% Nafion 117 alcoholic water solution to Nafion, and the electrolytic solution was produced. It stirred heating an electrolytic solution at 40 degrees C, and the condition as it is was held for 120 minutes. On slide glass, with the applicator, the electrolytic solution after stirring was cast so that the thickness after desiccation might be set to 30 micrometers, and the electrolyte sheet was formed. After making it harden at a room temperature for 24 hours, it exfoliated from the glass substrate and the sheet was heat-treated at the temperature of 50 degrees C for 3 hours. Furthermore, the film after desiccation was immersed in 1M sulfuric acid for 8 hours, after performing sufficient rinsing, it was made to season naturally, and the electrolyte membrane was obtained.

[0041] Next, what added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts, and was kneaded in the shape of a paste was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. the amount of platinum support of the obtained anode -- about 0.5 mg/cm2 -- it is -- the amount of ruthenium support -- about 0.5 mg/cm2 it was . The electrolyte membrane / electrode zygote was produced by adding the Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts to the field of the opposite hand of the formed electrolyte membrane, applying to it what was kneaded in the shape of a paste so that the thickness at the time of desiccation may be set to 15 micrometers, drying to it at 60 degrees

C for 3 hours, and forming a cathode in it. The amounts of platinum support of the obtained cathode were about 0.3 mg/cm2. The zygote after desiccation was immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.

[0042] (Example 1 of a comparison) The electrolyte membrane / electrode zygote which consists of perfluorocarbon-sulfonic-acid system ingredients as an example 1 of a comparison are explained below.

[0043] What added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts on 60mmx60mm Nafion 112 film which performed protonation processing, and was kneaded in the shape of a paste on it was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. The amounts of platinum support of the obtained anode were about 0.5 mg/cm2, and the amounts of ruthenium support were about 0.5 mg/cm2. The electrolyte membrane / electrode zygote was produced by adding the Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts to the field of the opposite hand of the formed electrolyte membrane, applying to it what was kneaded in the shape of a paste so that the thickness at the time of desiccation may be set to 15 micrometers, drying to it at 60 degrees C for 3 hours, and forming a cathode in it. The amounts of platinum support of the obtained cathode were about 0.3 mg/cm2. The zygote after desiccation was immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.

[0044] (Example 2 of a comparison) The production approach of a tungstic oxide hydrate / perfluorocarbon-sulfonic-acid electrolyte membrane and an electrolyte membrane / electrode zygote is explained below as an example 2 of a comparison.

[0045] It is tungstic oxide 1 / 3 hydrate to Nafion to a 5wt% Nafion 117 alcoholic water solution 4.5wt(s)% It added and the electrolytic solution was produced. It stirred heating an electrolytic solution at 40 degrees C, and the condition as it is was maintained for 120 minutes. On slide glass, with the applicator, the electrolytic solution after stirring was cast so that the thickness after desiccation might be set to 30 micrometers, and the electrolyte sheet was formed. After making it harden at a room temperature for 24 hours, it exfoliated from the glass substrate and the sheet was heat-treated at the temperature of 50 degrees C for 3 hours. Furthermore, the film after desiccation was immersed in 1M sulfuric acid for 8 hours, after performing sufficient rinsing, it was made to season naturally, and the electrolyte membrane was obtained.

[0046] Next, what added 5% of the weight of the Nafion-alcoholic solution with which the amount of electrolytes is equivalent to platinum and a ruthenium support carbon catalyst with dry weight at 60wt(s)% of the amount of catalysts, and was kneaded in the shape of a paste was applied in 30mmx30mm size on the electrolyte membrane of the 60mmx60mm size obtained above, it dried at 60 degrees C for 3 hours, and the anode was formed. the amount of platinum support of the obtained anode -- about 0.5 mg/cm2 -- it is -- the amount of ruthenium support -- about 0.5 mg/cm2 it was . The Nafion-alcoholic solution of an amount with which Nafion is equivalent to a platinum support carbon powder catalyst with dry weight at 60wt(s)% of the amount of catalysts was added to the field of the opposite hand of the formed electrolyte membrane, what was kneaded in the shape of a paste was applied to it so that the thickness at the time of desiccation might be set to 15 micrometers, and it might lap with an anode, and it dried to it at 60 degrees C for 3 hours, the cathode was formed in it, and the electrolyte membrane / electrode zygote was produced. The amounts of platinum support of the obtained cathode were about 0.3 mg/cm2. The zygote after desiccation was immersed in 1M sulfuric acid for 8 hours, and the electrolyte membrane / electrode zygote which was made to season naturally after performing sufficient rinsing, and protonated were obtained.

[0047] The electrolyte membrane / electrode zygote produced in examples 1-4 and the examples 1-2 of a comparison were inserted with the two carbon separator, and the cel for assessment of the structure shown in drawing 1 was assembled. the inside of drawing 1 , and a sign 1 -- an electrolyte membrane and 2 -- for an anode separator and 5, as for anode gas passage and 7, a cathode separator and 6 are [an anode and 3 / a cathode and 4 / a cathode gas passageway and 8] sealants. A methanol water solution is supplied to the anode of this cel 15%, air is supplied to a cathode, and it is current density 50 mA/cm2. The generation-of-electrical-energy trial was performed. The generation-of-electrical-energy electrical potential difference of each cel is shown in drawing 2 .

[0048] The example 1 of a comparison is 0.48V at the above-mentioned conditions. The electrical potential difference was obtained. Moreover, the example 2 of a comparison is almost equivalent 0.46V. The

electrical potential difference was measured.
[0049] on the other hand -- the cel electrical potential difference of an example 1 -- 0.63V it was . When this makes an electrolyte membrane distribute a metallic-oxide hydrate, the restraint of the water in the film increases, and as a result of an interaction's arising also in the methanol which is dissolving in water, the amount of methanols which moves to a cathode and is penetrated from an anode decreases. If the methanols to cross decrease in number, polarization produced by the direct reaction of a methanol can be controlled with a cathode, and it thinks for a cel electrical potential difference to improve as a result.
[0050] When the result of the example 2 of a comparison was considered, even if it was the same metallic-oxide hydrate, when the hydration numbers differed, it turned out that the water restraint described above changes and it is in the inclination to receive effect in methanol permeability as a result. With the ingredient shown in this example, it became clear that it had sufficient methanol cutoff nature effectiveness as a hydration number is five or less [1/2 or more] as a result of a detailed examination.
[0051] the electrical potential difference of the cel using the electrolyte membrane / electrode zygote of an example 2 -- 0.64V it was . As a result of influencing the methanol which had the restraint of a water molecule and has been hydrated also about the titanium oxide acid hydrate used in the example 2 and raising membranous methanol cutoff nature, it turned out that the improvement in a cel electrical potential difference is possible.
[0052] the cel electrical potential difference of an example 3 -- 0.68V it was . Although the example 3 uses the stannic-acid ghost hydrate as a metallic-oxide hydrate, as a result of the restraint by the metallic oxide influencing more powerfully and methanol cutoff nature's also increasing the hydration methanol molecule which was supplied to the anode since the adsorption power/restraint of the water in the film were relatively strong, and permeated into the film further as compared with the tungstic oxide hydrate used in the example 1, it can be judged that a cel electrical potential difference improves.
[0053] the cel electrical potential difference of an example 4 -- 0.70V it was . Although the electrical potential difference of an example 4 is improving rather than the example 1, this can be considered because the metallic-oxide hydrate contained in the electrolyte membrane of an example 4 is making it increase to 30wt(s)%. Since the absolute magnitude of the water restrained in the film increased, the amount of transparency of a methanol decreased by the interaction and methanol cutoff nature improved seemingly when there were many content rates of a metal hydrate oxide, it thinks.
[0054] The content of a metal hydrate oxide has methanol cutoff nature, i.e., a cel electrical potential difference, and a correlation, as shown in an example 4, and a cel electrical potential difference's tends to improve, so that content increases. This appeared in the result more than from 1wt% as an amount of metallic-oxide hydrates.
[0055] On the other hand, if a metallic-oxide hydrate is made into high content, a physical hole will produce the opening formed by particles in an electrolyte membrane, without the ability finishing burying an organic material. If a hole is generated, mechanical strength will fall selectively and it will become the cause of a crack (divide). If a crack arises in an electrolyte membrane, a methanol will cross a direct cathode. It turned out that less than [more than 5wt%80wt%] is more desirable than a detailed examination result as content of a metallic-oxide hydrate.
[0056] It turned out that a cel electrical potential difference can improve since reduction of the amount of crossovers of a methanol is attained when this electrolyte membrane is used for the fuel cell of the type which supplies the gas by which the electrolyte membrane which made the organic material which has proton conductivity from the above result distribute the metallic-oxide hydrate that hydration number of whose is 1/2 to 5 per monad is excellent in the methanol operating characteristic, a methanol water solution is included in an anode and it includes oxygen in a cathode. Moreover, since especially the proton conductivity ingredient of this invention is producible in a low-temperature process, industrial application expansion tends to plan it.
[0057] With this gestalt, the electrolyte membrane with which a hydration number consists of an ingredient which made the organic material which has proton conductivity distribute the metallic-oxide hydrate which is 1/2 to 5 per monad has the outstanding methanol cutoff capacity. When the electrolyte membrane using an ingredient is used for a methanol direct mold fuel cell and generated, a higher cel electrical potential difference can be realized as compared with the electrolyte membrane which consists of the conventional fluorine system ingredient.
[0058]
[Effect of the Invention] In this invention, the proton conductivity film producible in a low-temperature process 100 degrees C or less can be offered.

[Translation done.]

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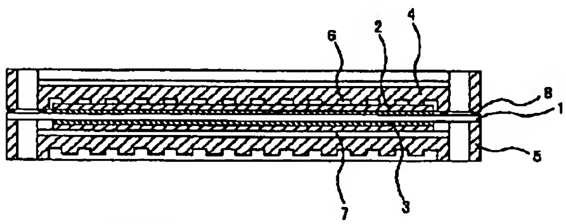
DRAWINGS

[Drawing 1]

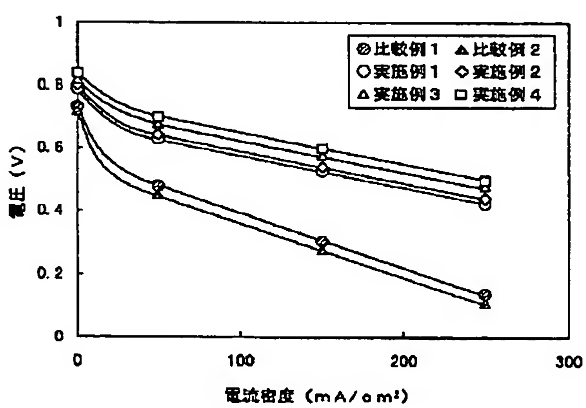
図 1



1…電解質膜　2…アノード　3…カソード
4…アノードセパレータ　5…カソードセパレータ
6…アノードガス流路　7…カソードガス流路
8…シール材

[Drawing 2]

図 2



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(71)出願人 000005108
株式会社日立製作所
東京都千代田区神田駿河台四丁目6番地

(72)発明者 山賀 賢史
茨城県日立市大みか町七丁目1番1号 株式会社日立製作所日立研究所内

(72)発明者 加茂 友一
茨城県日立市大みか町七丁目1番1号 株式会社日立製作所日立研究所内

(74)代理人 100075096
弁理士 作田 康夫

最終頁に続く

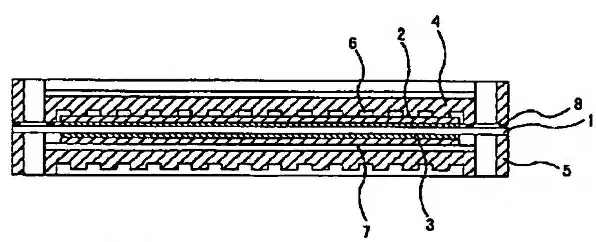
(54)【発明の名称】 プロトン伝導性材料

(57)【要約】

【課題】従来の燃料電池用電解質材料はメタノールが透過するため、クロスオーバーが生じていた。

【解決手段】その水和数が一分子あたり1／2から5である金属酸化物水和物とプロトン伝導性を有する有機材料を含み、有機材料に金属酸化物水和物が分散しているプロトン伝導性材料を作製することでメタノール遮断性が向上し、メタノールを含有する燃料をアノードに供給する燃料電池に用いた場合、クロスオーバーによるセル電圧低下を抑えることができる。

図 1



1…電解質膜　2…アノード　3…カソード
4…アノードセパレータ　5…カソードセパレータ
6…アノードガス流路　7…カソードガス流路
8…シール材

【特許請求の範囲】

【請求項１】金属酸化物水和物とプロトン伝導性を有する有機材料とを含み、該有機材料に該金属酸化物水和物が分散している材料であって、金属酸化物１分子あたりの水和数が１／２以上５以下であることを特徴とするプロトン伝導性材料。

【請求項２】金属酸化物水和物がＳｎ，Ｔｉ，Ｗの少なくとも一つの元素を含有することを特徴とする請求項１記載のプロトン伝導性材料。

【請求項３】金属酸化物水和物がプロトン伝導性を有する有機材料に対し５以上８０ｗｔ％以下の含有率であることを特徴とする請求項１記載のプロトン伝導性材料。

【請求項４】電気化学的酸化還元反応が進行する反応場であるところのアノードとカソードと電解質膜とからその基本材料が形成される燃料電池において、電解質膜が請求項１に示されるプロトン伝導性材料であることを特徴とする燃料電池。

【請求項５】１分子あたりの水和数が１／２以上５以下である金属酸化物水和物を作製する工程と、作製した金属酸化物水和物をプロトン伝導性を有する有機材料と混合する工程と、金属酸化物水和物とプロトン伝導性有機材料の混合物をシート状に形成する工程とを含むことを特徴とするプロトン伝導性材料の作製方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は水素あるいは炭化水素材料を燃料，酸素を含むガスを酸化剤ガスとして電気化学反応を利用してエネルギーを取り出す発電デバイスに関する技術分野に関するものである。

【０００２】

【従来の技術】最近の電子技術の進歩によって、電話器，ブックタイプパーソナルコンピュータ，オーデイオ・ビジュアル機器、或いはモバイル用情報端末機器などが小型化され、携帯用電子機器として急速な普及が進んでいる。従来こうした携帯用電子機器は二次電池によって駆動するシステムであり、シール鉛バッテリーからＮｉ／Ｃｄ電池，Ｎｉ／水素電池、更にはＬｉイオン電池へと新型二次電池の出現、小型化／軽量化及び高エネルギー密度化技術によって発展してきた。何れの二次電池においてもエネルギー密度を高めるための電池活物質開発や高容量電池構造の開発が行われ、より一充電での使用時間の長い電源を実現する努力が払われている。

【０００３】しかしながら、二次電池は一定量の電力使用後には充電することが必須であり、充電設備と比較的長い充電時間が必要となるために携帯用電子機器の長時間連続駆動には多くの問題が残されている。今後、携帯用電子機器は増加する情報量とその高速化に対応してより高出力密度で高エネルギー密度の電源、即ち連続使用時間の長い電源を必要とする方向に向かっており、充電を必要としない小型発電機（マイクロ発電機）の必要性が高まっている。

【０００４】こうした要請に対応するものとして燃料電池電源が考えられる。燃料電池は燃料の持つ化学エネルギーを電気化学的に直接電気エネルギーに変換するもので、通常のエンジン発電機などの内燃機関を用いた発電機のような動力部を必要としないため、小型発電デバイスとしての実現性は高い。

【０００５】又、燃料電池は燃料を補給する限り発電を継続するために、二次電池の場合に見られるような充電のために一時携帯用電子機器の動作を停止するということが不要となる。このような要請の中でパーフルオロカーボンスルホン酸系樹脂の電解質膜を用いてアノードで水素ガスを酸化し、カソードで酸素を還元して発電する固体高分子型燃料電池（ＰＥＦＣ：Polymer Electrolyte Fuel Cell）は出力密度が高い電池として知られている。

【０００６】ＰＥＦＣは水素燃料として用いるが、水素ガスの直接の取り扱いは安全面に問題がある。そこで燃料としてアルコールなどの炭化水素系燃料を用い、改質反応により水素を生成させ、得られた水素を燃料電池に供給するシステムが考えられている。このシステムでは燃料の取り扱いが容易で燃料供給インフラも水素に比較すると実用的であるが、改質反応は２５０℃以上の熱が必要とされることから携帯用途には不向きである。

【０００７】そこで、燃料に液体アルコールを用いて直接燃料電池に供給するタイプの検討が進められている。このタイプの燃料電池はメタノール直接型燃料電池（DMFC：Direct Methanol Fuel Cell ）と呼ばれている。液体燃料を直接利用できれば高温を必要とする改質器が不要となり、システムの軽量およびシンプル化が達成されるため特にモバイル機器の電源として有望視されている。

【０００８】しかしながら前述した、電解質材料であるところのパーフルオロカーボンスルホン酸系樹脂はメタノールを吸収する度合いが大きく、メタノールを吸収した樹脂は膨潤により形状が変化する。パーフルオロカーボンスルホン酸系樹脂をフィルム状にした場合メタノールに対する遮断性は低く、片面に接触させたメタノールは膜を浸透し裏側の面に透過してしまう。

【０００９】この材料をＤＭＦＣの電解質材料として用いた場合、燃料極であるアノードに供給したメタノールは膜に浸透・膨潤する結果、アノードから酸素極であるカソードへ透過する。透過したメタノールがカソードに到達するとカソードに供給された酸素と直接酸化反応が生じるため電気化学反応によって取り出せるエネルギーが減少する。その結果、電池としての発電電圧が低下する。

【００１０】よってＤＭＦＣの性能を向上させるためにはメタノール遮断性の優れた電解質材料の開発が必要となっていた。

【００１１】この課題に関し特開２００１－１６７７７５号では電解質膜を層状構造としイオン電導性の低い層を表面層にすることでメタノール遮断性に優れた電解質膜の提案を行っている。また特開平１０－４０９３６号公報では、イオン交換膜中にメタノールを酸化させるための酸化触媒層を埋設することでメタノールの対極への浸透を抑制した構造を提案している。

【００１２】しかし上記に示す手法による作製した電解質膜は層状構造となるため膜の薄型化に対する対応が困難であり、通常の均一膜に比較して製作工数が増加するといった課題もあった。

【００１３】また例えば特開２００１－９３５４３号ではメタノールクロスオーバーを防止するためＯＨ基を含有したガラス状非晶質プロトン伝導体を有機材料に分散させた材料を提案している。しかしながら上記に示す材料はそのＯＨ基を有する材料を作製する工程上、５００℃以上の高温加熱処理が必要であり低温プロセスによる材料作製は非常に困難であった。

【００１４】

【発明が解決しようとする課題】本発明は従来のフッ素系に比較してメタノール遮断性が向上したプロトン伝導性膜を提供することにある。また、１００℃以下の低温プロセスで作製可能なプロトン伝導性膜およびそれを電解質材料として使用した燃料電池等の提供にある。

【００１５】

【課題を解決するための手段】本発明では前述の課題を達成するために鋭意検討を推し進め、プロトン伝導性を有する有機材料にその水和数が一分子あたり１／２から５である金属酸化物水和物を添加・分散させることにより電解質膜を形成すると、メタノール遮断性が大いに向上するとの知見を得るに至った。

【００１６】金属酸化物水和物は層間水あるいは吸着水を有し、ある種の金属酸化物水和物のそれらに対する拘束力あるいは相互作用力は非常に強い。

【００１７】この拘束力は、燃料電池のアノードで生成したプロトンが膜中を移動する際に随伴する水分子であるところのプロトン随伴水にも影響を与える。つまり金属酸化物水和物が分散状態で電解質膜中に存在するとその中を移動する水動きを抑制し、見かけ上、膜を浸透・透過する指標である水透過率を低下させる効果を示す。この場合、プロトンは拘束された水分子をホッピングして電荷を移動させるため、イオン伝導度も従来材料と同等程度である特徴を有する。

【００１８】金属酸化物水和物を分散させたイオン伝導性有機材料を電解質材料に用いて燃料電池を組み立て、燃料極であるアノードにメタノール水溶液を供給した場合、電解質膜中でメタノールに水和した水分子が金属酸化物によって拘束されるため、水和によって緩く結合しているメタノール分子にも影響が生じ、その結果として酸素極であるカソードに、膜を透過して到達するメタノールの量が減少する。すなわちメタノールクロスオーバー量が減少するため、ＤＭＦＣのセル電圧低下が抑制でき、良好な性能が発揮される。

【００１９】金属酸化物水和物の金属元素としてはＳｎ，Ｔｉ，Ｗ元素を少なくとも１種以上含有する材料が水分子の拘束力の観点から特に好ましい。またこの他にもＡｌ，Ｓｉ，Ｓｃ，Ｖ，Ｃｒ，Ｍｎ，Ｆｅ，Ｃｏ，Ｎｉ，Ｃｕ，Ｚｎ，Ｇａ，Ｇｅ，Ａｓ，Ｓｅ，Ｙ，Ｚｒ，Ｎｂ，Ｍｏ，Ｒｕ，Ｒｈ，Ｐｄ，Ａｇ，Ｉｎなどの遷移金属元素をはじめとする元素であっても問題ない。

【００２０】金属酸化物水和物の有機材料に対する含有率はメタノール透過率として実際に効果の現れる１ｗｔ％以上が望ましい。さらには電解質を組み入れた電池のセル電圧に影響の現れる５ｗｔ％以上であるとさらに望ましい。

【００２１】一方、金属酸化物水和物を高含有率にすると、粒子同士で形成する空隙を有機材料が埋めきれずに物理的な空孔が電解質膜に生じる。空孔が生じると部分的に機械強度が低下し、クラック（割れ）の原因となる。電解質膜にクラックが生じるとメタノールが直接カソードにクロスオーバーしてしまう。よって金属酸化物水和物の有機材料に対する含有率の上限としては８０ｗｔ％が望ましい。

【００２２】イオン伝導性を有する有機材料としては耐熱性，耐酸性，可撓性を有する材料であれば特に限定はないが、パーフルオロカーボンスルホン酸のほか、さらには化学修飾したポリスチレンやポリエーテルケトン，ポリエーテルエーテルケトン，ポリスルホン，ポリエーテルスルホンあるいは他のエンジニアリングプラスチック材料のスルホン酸，リン酸、その他のプロトンキャリアをドープあるいは化学的に結合，固定化した材料が好ましい。

【００２３】

【発明の実施の形態】以下実施例により本発明をさらに詳しく説明するが、本発明はこれらに限定されるものではない。

【００２４】（実施例１）本発明の実施例として酸化タングステン水和物／パーフルオロカーボンスルホン酸電解質膜および電解質膜／電極接合体の作製方法を以下に説明する。

【００２５】５℃に冷却した４５０ｍｌ３Ｎ ＨＣｌに、１．０Ｍ Na_2WO_3水溶液５０mlをマグネチックスターラーで撹拌しながら徐々に滴下し、黄色沈殿を得た。上澄み液を除いた後、０．１Ｎ ＨＣｌ ３００ｍｌを加えて１０分間撹拌し、沈殿を沈降させるため静置した後、上澄み液を取り除いた。

【００２６】続いて沈殿に３００ｍｌの純水を加え、１０分間撹拌した後、２４時間放置した。粉末が沈降し完全に分離状態となった溶液の上澄み液を捨て、新たに同量の純水を添加した。同様の洗浄操作を６回繰り返し、

未反応原料に由来する不純物イオンを取り除いた。その後濾過することにより酸化タングステン水和物を得た。本方法で作製した沈殿はＸ線回折測定，熱重量・示差熱分析より酸化タングステン２水和物であることが確認された。

【００２７】５ｗｔ％のナフィオン１１７アルコール水溶液（水，イソプロパノール，ノルマルプロパノールが重量比で２０：４０：４０の混合溶媒：Fluka Chemika社製)に酸化タングステン水和物をナフィオンに対し４．５ｗｔ％ 添加し、電解質溶液を作製した。電解質溶液を４０℃に加熱しながら攪拌し、そのままの状態を120分維持した。攪拌後の電解質溶液をスライドガラス上にアプリケータで乾燥後厚みを３０μｍとなるようにキャスティングし、電解質シートを形成した。室温で２４時間硬化させた後シートをガラス基板から剥離し、５０℃の温度で３時間加熱処理した。さらに乾燥後の膜を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させ電解質膜を得た。

【００２８】次に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオンーアルコール溶液を添加してペースト状に混練したものを上記で得られた６０㎜×６０㎜サイズの電解質膜上に３０㎜×３０㎜のサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０．５mg／cm²であり、ルテニウム担持量は約０．５mg／cm² であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィオンーアルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚みが１５μｍとなるようにアノードと重なるように塗布し、６０℃で３時間乾燥しカソードを形成し電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０．３mg／cm² であった。乾燥後の接合体を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００２９】（実施例２）本発明の実施例として酸化チタン水和物／パーフルオロカーボンスルホン酸電解質膜および電解質膜／電極接合体の作製方法を以下に説明する。金属チタン粉末５ｇを３０％過酸化水素水に反応させながら８０℃に加熱し、２４０時間攪拌・溶解させた後未反応物を濾過により取り除き前駆体となる過酸化物を作製した。

【００３０】得られた水溶液に５Ｎの苛性ソーダ（ＮａＯＨ）水溶液を加えた後、６Ｎ塩酸を加えて沈殿を得た。この沈殿物をろ過し、デシケータ中で乾燥させた。上記の方法で得られた乾燥粉末５ｇに４００ｍｌの純水を添加し３０分間攪拌し２４時間放置した。粉末が沈降し完全に分離状態となった溶液の上澄み液を捨て、新たに同量の純水を添加した。同様の洗浄操作を６回繰り返し、未反応原料に由来する不純物イオンを取り除き酸化チタン水和物を得た。熱重量測定から水和数は２であることが判明した。

【００３１】５ｗｔ％のナフィオン１１７アルコール水溶液に酸化チタン水和物をナフィオンに対し４．５ｗｔ％ 添加し、電解質溶液を作製した。電解質溶液を４０℃に加熱しながら攪拌し、そのままの状態を１２０分維持した。攪拌後の電解質溶液をスライドガラス上にアプリケータで乾燥後厚みを３０μｍとなるようにキャスティングし、電解質シートを形成した。室温で２４時間硬化させた後シートをガラス基板から剥離し、５０℃の温度で３時間加熱処理した。さらに乾燥後の膜を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させ電解質膜を得た。

【００３２】次に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオンーアルコール溶液を添加してペースト状に混練したものを上記で得られた６０㎜×６０㎜サイズの電解質膜上に３０㎜×３０㎜のサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０．５mg／cm²であり、ルテニウム担持量は約０．５mg／cm² であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィオンーアルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚さが１５μｍとなるようにアノードと重なるように塗布し、６０℃で３時間乾燥しカソードを形成し電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０．３mg／cm²であった。乾燥後の接合体を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００３３】（実施例３）本発明のもう一つの実施例として酸化スズ水和物／スルホン化ポリエーテルスルホン電解質膜、および電解質膜／電極接合体の作製方法を以下に説明する。

【００３４】塩化第二スズ($SnCl_4 \cdot 5H_2O$) １７．５ｇを５０ｍｌの水に溶解して６０℃に加熱して加水分解した。これにアンモニア水を加えて９５℃で１時間加熱，熟成し、得られた沈殿物をろ過し、乾燥させてスズ酸化物水和物（$SnO_2 \cdot nH_2O$）を得た。熱重量変化測定からｎは約１．８ と見積もられた。作製した酸化スズ水和物１０ｇに４００ｍｌの純水を添加し３０分間攪拌し２４時間放置した。沈降，分離した酸化スズ水和物の上澄み液を採取して捨て、新たに同量の純水を添加した。同様の洗浄操作を６回繰り返し、未反応原料に由来する不純物イオンを取り除いた。洗浄処理の後自然乾燥させ以降の電解質膜作製に用いた。

【００３５】乾燥処理したポリエーテルスルホン０．５ｇ をＮＭＰ(Ｎ－メチルピロリドン)に添加し、２５℃

で２時間攪拌し、５ｗｔ％溶液を作製した。この溶液に硫酸４５ｍｌを加え、不活性ガス雰囲気下４５℃で３時間加熱攪拌した。反応容器ごと１５℃のウォーターバスに入れさらに発煙硫酸２０ｍｌを１ｍｌ／分の割合で添加し、さらに添加終了後も１．５ 時間連続攪拌しスルホン化反応を進行させた。得られた溶液５ｍｌにつき２リットルの割合の純水に滴下し、スルホン化ポリエーテルスルホンを析出させた。得られた析出沈殿はろ過，純水による洗浄のあと乾燥させ、スルホン化ポリエーテルスルホンを得た。得られたスルホン化ポリエーテルスルホンのイオン交換容量は１．２５meq／ｇであった。上記方法で作製したスルホン化ポリエーテルスルホンを水，イソプロパノール，ノルマルプロパノールが重量比で２０：４０：４０の混合溶媒に溶解させ２０ｗｔ％溶液を調整した。

【００３６】上記方法で作製した酸化スズ水和物を２０ｗｔ％スルホン化ポリエーテルスルホン溶液に、スルホン化ポリエーテルスルホンに対して４．５ｗｔ％ になるように添加し、電解質溶液を作製した。電解質溶液を常温にて１２０分間攪拌した。攪拌後の電解質溶液をスライドガラス上にアプリケータで乾燥後厚みを３０μｍとなるようにキャステイングし電解質シートを形成した。室温で２４時間保持させた後、５０℃の温度で３時間加熱処理した。その後シートを基板から剥離させ、充分な水洗を行ったのちに自然乾燥させ電解質膜を得た。

【００３７】次に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオン－アルコール溶液を添加してペースト状に混練したものを上記で得られた６０㎜×６０㎜サイズの電解質膜上に３０㎜×３０㎜のサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０．５mg／cm²であり、ルテニウム担持量は約０．５mg／cm² であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィオン－アルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚さが１５μｍとなるように塗布して６０℃で３時間乾燥しカソードを形成することにより電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０．３mg／cm²であった。乾燥後の接合体を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００３８】（実施例４）本発明のもう１つの実施例を以下に説明する。

【００３９】塩化第二スズ($SnCl_4・5H_2O$) １７．５ｇを５０ｍｌの水に溶解して６０℃に加熱して加水分解した。これにアンモニア水を加えて９５℃で１時間加熱，熟成し、得られた沈殿物をろ過し、乾燥させてスズ酸化物水和物（$SnO_2・nH_2O$）を得た。熱重量変化測定からｎは約１．８と見積もられた。作製した酸化スズ水和物１０ｇに４００ｍｌの純水を添加し３０分間攪拌し２４時間放置した。沈降，分離した酸化スズ水和物の上澄み液を採取して捨て、新たに同量の純水を添加した。同様の洗浄操作を６回繰り返し、未反応原料に由来する不純物イオンを取り除いた。洗浄処理ののち自然乾燥させ以降の電解質膜作製に用いた。

【００４０】上記方法で作製した酸化スズ水和物を５ｗｔ％のナフィオン１１７アルコール水溶液にナフィオンに対して３０ｗｔ％量になるように添加し，電解質溶液を作製した。電解質溶液を４０℃に加熱しながら攪拌し、そのままの状態を１２０分保持した。攪拌後の電解質溶液をスライドガラス上にアプリケータで乾燥後厚みを３０μｍとなるようにキャステイングし電解質シートを形成した。室温で２４時間硬化させた後シートをガラス基板から剥離し、５０℃の温度で３時間加熱処理した。さらに乾燥後の膜を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させ電解質膜を得た。

【００４１】次に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオン－アルコール溶液を添加してペースト状に混練したものを上記で得られた６０㎜×６０㎜サイズの電解質膜上に３０㎜×３０㎜のサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０．５mg／cm²であり、ルテニウム担持量は約０．５mg／cm² であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィオン－アルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚さが１５μｍとなるように塗布して６０℃で３時間乾燥しカソードを形成することにより電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０．３mg／cm²であった。乾燥後の接合体を１Ｍ硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００４２】（比較例１）比較例１としてパーフルオロカーボンスルホン酸系材料から構成される電解質膜／電極接合体を以下に説明する。

【００４３】プロトン化処理を行った６０㎜×６０㎜ナフィオン１１２膜に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオン－アルコール溶液を添加してペースト状に混練したものを上記で得られた６０㎜×６０㎜サイズの電解質膜上に３０㎜×３０㎜のサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０．５mg／cm²であり、ルテニウム担持量は約０．５mg／cm²であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィ

オンーアルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚さが１５μmとなるように塗布して６０℃で３時間乾燥しカソードを形成することにより電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０.３mg／cm^{2}であった。乾燥後の接合体を１M硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００４４】（比較例２）比較例２として酸化タングステン水和物／パーフルオロカーボンスルホン酸電解質膜および電解質膜／電極接合体の作製方法を以下に説明する。

【００４５】酸化タングステン１／３水和物を、５ｗｔ％のナフィオン１１７アルコール水溶液に、ナフィオンに対し４.５ｗｔ％ 添加し電解質溶液を作製した。電解質溶液を４０℃に加熱しながら撹拌し、そのままの状態を１２０分維持した。撹拌後の電解質溶液をスライドガラス上にアプリケータで乾燥後厚みを３０μmとなるようにキャステイングし、電解質シートを形成した。室温で２４時間硬化させた後シートをガラス基板から剥離し、５０℃の温度で３時間加熱処理した。さらに乾燥後の膜を１M硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させ電解質膜を得た。

【００４６】次に、白金・ルテニウム担持炭素触媒に乾燥重量で電解質量が触媒量の６０ｗｔ％に相当する５重量％のナフィオンーアルコール溶液を添加してペースト状に混練したものを上記で得られた６０mm×６０mmサイズの電解質膜上に３０mm×３０mmのサイズで塗布し６０℃で３時間乾燥してアノードを形成した。得られたアノードの白金担持量は約０.５mg／cm^{2}であり、ルテニウム担持量は約０.５mg／cm^2 であった。形成された電解質膜の反対側の面に、白金担持炭素粉末触媒に乾燥重量でナフィオンが触媒量の６０ｗｔ％に相当する量のナフィオンーアルコール溶液を添加し、ペースト状に混練したものを乾燥時の厚みが１５μmとなるようにアノードと重なるように塗布し、６０℃で３時間乾燥しカソードを形成し電解質膜／電極接合体を作製した。得られたカソードの白金担持量は約０.３mg／cm^{2}であった。乾燥後の接合体を１M硫酸に８時間浸漬し、充分な水洗を行ったのちに自然乾燥させプロトン化を施した電解質膜／電極接合体を得た。

【００４７】実施例１～４および比較例１～２で作製した電解質膜／電極接合体を２枚のカーボンセパレータで挟み、図１に示す構造の評価用セルを組み立てた。図１中、符号１は電解質膜、２はアノード、３はカソード、４はアノードセパレータ、５はカソードセパレータ、６はアノードガス流路、７はカソードガス流路、８はシール材である。このセルのアノードに１５％メタノール水溶液を、カソードに空気を供給し電流密度５０ｍＡ／cm^2 で発電試験を行った。図２に各セルの発電電圧を示す。

【００４８】比較例１は上記条件で０.４８Ｖ の電圧が得られた。また比較例２はほぼ同等の０.４６Ｖ の電圧が計測された。

【００４９】一方実施例１のセル電圧は０.６３Ｖ であった。これは電解質膜に金属酸化物水和物を分散させることにより膜中の水の拘束力が増加し、水に溶解しているメタノールにも相互作用が生じる結果、アノードからカソードへ移動，透過するメタノール量が減少する。クロスオーバーするメタノールが減少するとカソードでメタノールの直接反応により生ずる分極を抑制でき、その結果セル電圧が向上するためと考えられる。

【００５０】比較例２の結果を考察すると同じ金属酸化物水和物であってもその水和数が異なると、上記で述べた水拘束力が変化し、結果としてメタノール透過性に影響を受ける傾向にあることが分かった。詳細な検討の結果、本実施例に示した材料では水和数は１／２以上５以下であると、充分なメタノール遮断性効果を有することが判明した。

【００５１】実施例２の電解質膜／電極接合体を用いたセルの電圧は０.６４Ｖ であった。実施例２で用いた酸化チタン酸水和物についても水分子の拘束力を有し、水和しているメタノールに影響して膜のメタノール遮断性を向上させる結果、セル電圧向上が可能であることが分かった。

【００５２】実施例３のセル電圧は０.６８Ｖ であった。実施例３は金属酸化物水和物としてスズ酸化物水和物を用いているが、実施例１で用いた酸化タングステン水和物に比較して膜中の水の吸着力／拘束力が相対的に強いため、アノードに供給され、さらに膜中に浸透した水和メタノール分子も金属酸化物による拘束力がより強力に影響し、メタノール遮断性が増す結果、セル電圧が向上すると判断できる。

【００５３】実施例４のセル電圧は０.７０Ｖ であった。実施例４は実施例１よりも電圧が向上しているが、これは実施例４の電解質膜に含有されている金属酸化物水和物が３０ｗｔ％に増加させているためと考えることができる。金属水和物酸化物の含有割合が多いと膜中で拘束される水の絶対量が増え、その相互作用によりメタノールの透過量が減少し、見かけ上メタノール遮断性が向上したためと考えられる。

【００５４】金属水和物酸化物の含有率は実施例４に示されるようにメタノール遮断性、つまりセル電圧と相関関係があり、含有率が増加するほどセル電圧も向上する傾向がある。これは金属酸化物水和物量として１ｗｔ％以上から結果に表れた。

【００５５】一方、金属酸化物水和物を高含有率にすると、粒子同士で形成する空隙を有機材料が埋めきれずに物理的な空孔が電解質膜に生じる。空孔が生じると部分的に機械強度が低下し、クラック（割れ）の原因とな

る。電解質膜にクラックが生じるとメタノールが直接カソードにクロスオーバーしてしまう。金属酸化物水和物の含有率としては、詳細な検討結果より５ｗｔ％以上８０ｗｔ％以下が望ましいことが分かった。

【００５６】以上の結果よりプロトン伝導性を有する有機材料にその水和数が一分子あたり１／２から５である金属酸化物水和物を分散させた電解質膜はメタノール遮断特性が優れており、アノードにメタノール水溶液をカソードに酸素を含むガスを供給するタイプの燃料電池にこの電解質膜を用いた場合、メタノールのクロスオーバー量の減少が可能となるためにセル電圧が向上できることが分かった。また特に本発明のプロトン伝導性材料は、低温プロセスで作製可能であるため工業的な応用展開が図りやすい。

【００５７】本形態では、水和数が一分子あたり１／２から５である金属酸化物水和物をプロトン伝導性を有する有機材料に分散させた材料からなる電解質膜は優れたメタノール遮断能力を有する。材料を用いた電解質膜をメタノール直接型燃料電池に用いて発電した場合、従来のフッ素系材料からなる電解質膜に比較しより高いセル電圧を実現することができる。

【００５８】

【発明の効果】本発明では１００℃以下の低温プロセスで作製可能であるプロトン伝導性膜を提供できる。

【図面の簡単な説明】

【図１】本発明に関わる固体高分子型積層燃料電池の単位構成を示す図である。

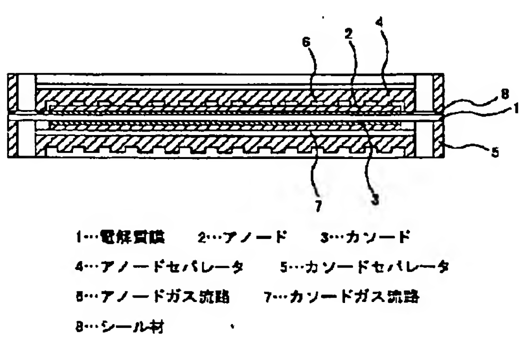
【図２】本発明に関わる材料からなる電解質膜を用いたメタノール直接型燃料電池の電流密度とセル電圧の関係を示す結果を示す図である。

【符号の説明】

１…電解質膜、２…アノード、３…カソード、４…アノードセパレータ、５…カソードセパレータ、６…アノードガス流路、７…カソードガス流路、８…シール材。

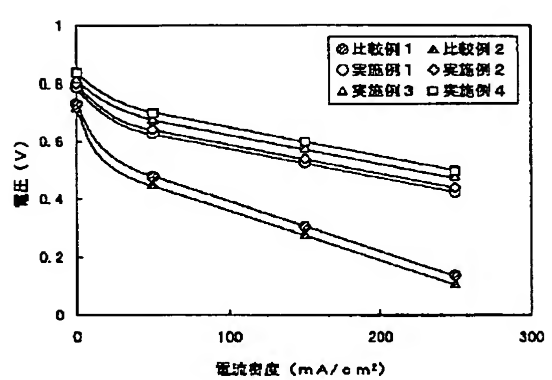
【図１】

図 1



【図２】

図 2



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